

4H- to 3C-SiC Polytypic Transformation During Oxidation

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Abstract: The formation of single and multiple stacking faults that sometimes give rise to 3C-SiC was observed in a highly doped n-type 4H-SiC epilayer following thermal oxidation. Transmission electron microscopy following oxidation revealed single stacking faults and bands of 3C-SiC within a 4H-SiC matrix in the epilayer. In addition to the 3.22 eV photon energy peak corresponding to 4H-SiC, depth-resolved cathodoluminescence spectroscopy at 25 °C based on low energy-excited electron nanoscale luminescence revealed a spectral peak at 2.5 eV photon energy that was not present in the sample prior to oxidation. The polytypic transformation is tentatively attributed to the motion of Shockley partial dislocations on parallel (0001) slip planes. The generation and motion of these partials may have been induced by the stresses that were generated during oxidation, and/or the epilayer stresses generated by change in lattice constant due to its heavy doping.

Introduction

Single crystal 4H-SiC is currently the polytype of choice for the fabrication of silicon carbide high power devices, including prototype power metal oxide semiconductor field effect transistors. This is largely due to its high electron mobility and the near isotropy of the mobility in directions parallel and perpendicular to the crystallographic *c*-axis. Considerable progress has been made toward the improvement of the gate oxide quality [1] in terms of reducing interface traps and improving inversion channel mobility, and also in the reduction of 4H-SiC crystal defect density [2]. However, little investigation has been conducted to understand how thermally induced surface and sub-surface modification impacts device electrical characteristics. The polymorphic nature of SiC raises the possibility that structural relaxation, i.e., polytype phase transitions, can occur under certain conditions. Previously, it has been shown that phase changes may occur in SiC under applied thermomechanical stress [3]. Pirouz *et al.* have shown polytypic transformation to occur in single crystal SiC when subjected to external mechanical loading [4] while Vlaskina and Shin [5] induced 6H-SiC to 3C-SiC polytypic transformation under vacuum conditions at temperatures between 1800 °C and 2000 °C.

In this work, we present results for interface states and structural changes due to extended polytype transformations at 4H-SiC surfaces and interfaces. In addition, we show that the energies observed via low energy electron-excited nanoscale luminescence (LEEN) spectroscopy are consistent with the structural features evident in cross sectional transmission electron microscopy (TEM). In studying the effects of oxidation on the surface and sub-surface of 4H-SiC of various doping levels to understand its effect on the electrical characteristics of metal/SiC contacts, we have observed 4H-SiC to 3C-SiC polytypic transformation in heavily doped ($1.7 \times 10^{19} \text{ cm}^{-3}$) epilayer samples.

Experimental

In order to carry out optical studies on metal-SiC contacts, we used representative contact overlayers of Ti/Pt that were thin enough to transmit significantly in the visible wavelength region. Pt/Ti/4H-SiC interfaces were formed by sputter deposition of 1-2 nm Ti followed by 2-3 nm Pt on chemically treated SiC samples all from the same wafer. The 4H-SiC wafers consisted of 2 μm thick, n-type ($N_d = 1.7 \times 10^{19} \text{ cm}^{-3}$) epilayer grown 8° off the basal (0001) plane on 4 $\Omega\text{-cm}$ p-type substrates. Our studies followed the same sequence of process steps used conventionally to remove surface contamination and structural damage prior to ohmic contact formation. This sequence of process steps was incorporated into the design of experiment shown in Fig 1. First, the sample was cleaned with acetone and methanol (henceforth termed 'SC'). After this solvent clean, the set was split in two with one sub-set put aside for bare surface X-ray photoelectron spectroscopy (XPS) and TEM analyses and the other to be metallized and analyzed by LEEN, XPS, and current-voltage (I-V) measurement (henceforth termed SCM). The remaining samples were dry oxidized at 1150°C for 4 h, after which the oxide was stripped with 49% HF acid and the surface rinsed with deionized (DI) water and then p-cleaned, which consists of 1:1 volume ratio of H_2SO_4 and H_2O_2 solution; henceforth these samples are termed OSP. This set was split in two with one sub-set put aside for bare surface analyses and the other half was metallized by the sputter deposition of Ti(1 nm)/Pt(2 nm) (this sub-set is henceforth termed OSPM) for LEEN, XPS, analyses and I-V measurements.

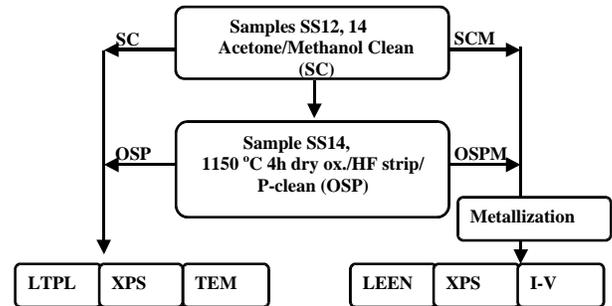


Fig.1: Experimental process sequence for the comprehensive study of oxidation-induced morphological and sub-surface modification of 4H-SiC epilayer.

Results and discussions

We used LEEN spectroscopy, a low energy form of cathodoluminescence spectroscopy (CLS) to characterize the energies of electronic states as a function of distance from the SiC interfaces [6]. CLS and LEEN spectroscopy involve the excitation of electron-hole pairs by an incident electron beam. The electron beam generates a cascade of secondary electrons that lose energy to plasmons and subsequently electron-hole pair creation. The optical signal results from radiative recombination of these free electrons and holes. Energy loss in electron cascade and, therefore excitation depth, U_0 , varies with incident beam voltage E_B . Figure 2a depicts the LEEN spectra of the metallized solvent cleaned sample. A 3.22 eV photon energy peak is observable at $E_B = 0.8 \text{ keV}$ ($U_0 = 6 \text{ nm}$, including the metal), which peaks more sharply at higher E_B with further penetration into the epilayer. This energy corresponds to the near band edge (NBE) emission of 4H-SiC, and it is the only such peak evident in this sample. Emission observed at lower photon energies corresponds to a broad

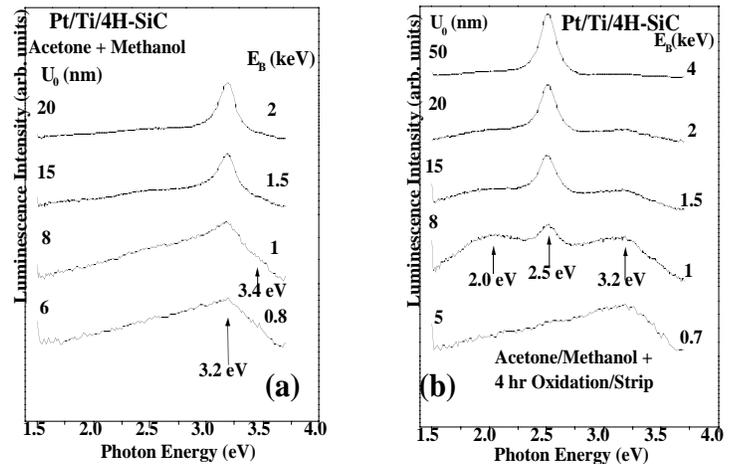


Fig. 2: CLS-LEEN spectra of a) solvent cleaned 4H-SiC sample depicts the 3.22 eV photon energy of 4H-SiC, and b) of 4H-SiC sample after OSPM. A sharp 2.5 eV photon peak extends at least 50 nm deep into the epilayer.

distribution of states in the band gap confined to the near-interface region. The spectra of the OSPM sample changed dramatically as shown in Fig. 2b. A sharp 2.5 eV photon peak appears at all excitation depths except $U_0 = 5$ nm and $E_B = 0.7$ keV from the metal/SiC interface, while a broad 3.2 eV photon peak slowly decays over the first 20 nm excitation depth. The 2.5 eV emission at all depths except $U_0 = 5$ nm indicates the occurrence of a substantial structural change in a large volume fraction of the oxidized 4H-SiC sample.

The cross sectional TEM image shown in Fig. 3a from the SC sample shows an undisturbed cross section, consistent with LEEN spectra to be 4H-SiC. However, after OSP the TEM image reveals a dramatic structural changes over the entire thickness of the epilayer as shown in Fig. 3b, which is also consistent with the dramatic changes observed by LEEN in Fig. 2b. Referencing from the surface, transformation bands of 3C-SiC can be seen to propagate into the 4H-SiC epilayer. High-resolution transmission electron microscopy (HRTEM) of Fig. 3c offers a closer look at one of the 3C bands. The image shows six Si-C bilayers representing the 3C-SiC stacking sandwiched between 4H-SiC.

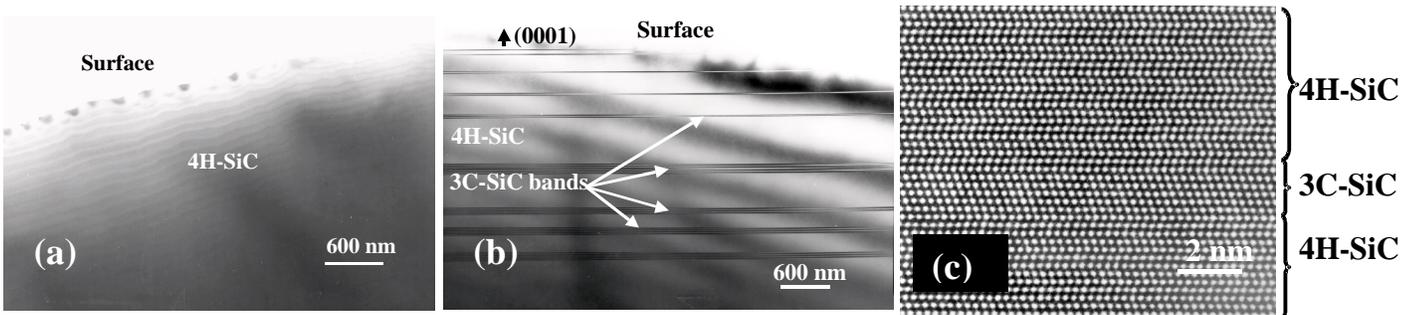


Fig. 3: XTEM shows a) the as received 4H-SiC with epilayer; b) 3C-SiC bands propagating parallel to the 8° -tilted basal plane after OSP; c) HRTEM image from a transformation band in (b) reveals that one of the 3C-SiC sub-bands to be made up of six Si-C bi-layers.

Multiple I-V measurements on the SCM sample, with a representative curve shown in Fig. 4a, depict it to be symmetrically non-ohmic, which can possibly be attributed to the presence of adventitious carbon compounds observed by XPS on bare surface SC samples [7]. The ohmic contact on the OSPM sample of Fig. 4b showed a substantial reduction in adventitious carbon when analyzed with XPS prior to metallization [7], which may offer an explanation for its linear behavior even without the traditional post-metal anneal. Alternatively, the presence of the 3C bands could also be a factor in obtaining linear I-V behavior.

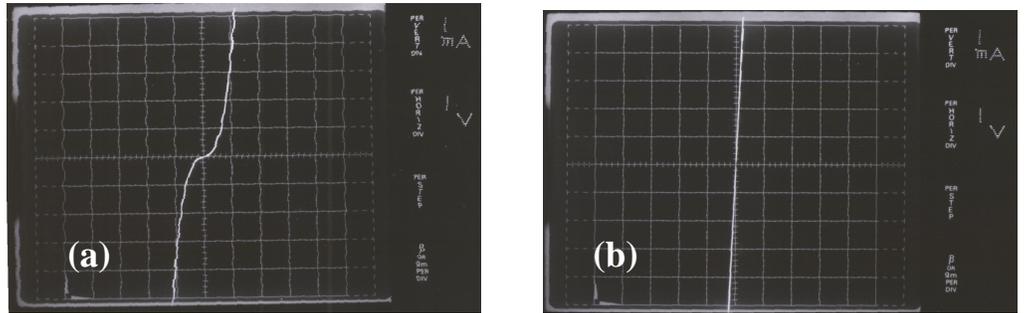


Fig. 4: Representative I-V characteristics on 4H-SiC of a) SCM sample exhibits rectifying characteristics and b) OSPM sample.

The discrepancy in photon energy between the observed 2.5 eV peak by LEEN and the usual bulk value of 2.39 eV corresponding to the 3C-SiC bandgap can be accounted for by quantum effects due to the thinness of the 3C bands. Comparison of band offsets for 3C-SiC versus 6H-SiC [8] and 4H-SiC versus 6H-SiC [9] provides cumulative 3C-SiC versus 4H-SiC values of $\Delta E_C = 0.84 \pm 0.1$ eV and $\Delta E_V = 0.07 \pm 0.1$ eV. Here, the conduction band of 3C-SiC lies lower in energy than that of 4H-SiC, whereas the valence bands almost align. In this case, the positive conduction band offsets result in quantum wells (QW) for electrons inside 3C band, but no confinement for holes. For a QW of width 1.75 nm, corresponding to two 3C unit cell repeat distances normal to the basal plane, the lowest energy state for electrons with $m_{\text{eff}} = 0.66m_0$ equals 0.11 eV from bottom of the well. NBE emission in this

structure would involve recombination of holes from the lowest QW state in the conduction band to the top of the valence band. The resulting emission would occur at 2.39 eV (3C-SiC bandgap) + 0.11 eV (QW ground energy state) = 2.5 eV, in excellent agreement with the LEEN spectra. Furthermore, since the quantum well is an efficient collector of free electrons, it serves as a more efficient source of carrier recombination. This accounts for the much stronger 3C-SiC NBE emission at 2.5 eV relative to that of 4H-SiC at 3.2 eV in Fig. 3b. The ultrathin nature of the 3C-SiC layers imbedded in 4H-SiC and the expected 3C-4H SiC band offsets indicate that these inclusions will form multiple quantum wells and should have a significant effect on the electrical characteristics of the contacts.

Conclusion

We have determined that single and multiple layers of stacking faults form in highly doped 4H-SiC at temperatures as low as 1150°C during thermal oxidation. In the cases where stacking faults form on neighboring (0001) planes, bands of 3C-SiC form the 4H→3C polytypic transformation. There is the possibility that the transformation may have resulted in the ohmic contact by a change in the band structure to that of 3C-SiC. We tentatively suggest that the observed stacking fault layers and polytypic transformation may be the result of nucleation and propagation of $\frac{1}{3}\langle 10\bar{1}0 \rangle$ Shockley partial dislocations on basal (0001) planes [3]. These may act as a mechanism of relieving the strain produced by the stresses due to heavy doping ($1.7 \times 10^{19} \text{ cm}^{-3}$) of the epilayer, perhaps assisted by stress nucleation at defects on the substrate surface. These results have significant implications for the design and fabrication of SiC electronic devices.

Acknowledgements

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